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(54) Gasoline composition.

(57) The invention provides a gasoline composition comprising a major amount of a gasoline and from 5 ppmw to 1,000 ppmw based on the gasoline composition of a mixture of (a) an oil soluble polyamine selected from the group consisting of (i) a defined aliphatic alkylene polyamine, (ii) a defined Mannich polyamine, and (iii) mixtures of (i) and (ii); and (b) an oil soluble hydrocarbyl poly(oxyalkylene) aminocarbamate having a number average molecular weight in the range from 600 to 10,000 having at least one basic nitrogen atom wherein said hydrocarbyl group contains from 1 to 30 carbon atoms, and wherein the weight ratio of said polyamine (a) to said hydrocarbyl poly(oxyalkylene) aminocarbamate (b) ranges from 3:1 to 1:2; and a gasoline additive concentrate containing said mixture.

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The present invention relates to a gasoline composition for use in an internal combustion engine and a gasoline additive concentrate.

Gasoline compositions have traditionally been formulated to improve the performance of carburettor and throttle body injected engines. Beginning in about 1984, electronic port fuel injected engines were commonly introduced by automobile manufacturers. Shortly thereafter, in about 1985, problems began to be reported with intake valve deposits in electronic port fuel injected engines characterised by hard starting, stalls, and stumbles during acceleration and rough engine idle.

Accordingly, it would be desirable to have fuel compositions which reduced or eliminated such undesirable intake valve deposits in electronic port fuel injected engines. Also, since some carburettor and throttle body injector engines will still be in use for the foreseeable future, it would be desirable if such fuels could also be compatible with these engines. Intake valve detergency is generally defined by the BMW NA standard of intake valve cleanliness for unlimited mileage, which is an established correlation of good driveability with average intake valve deposit weight of 100 milligrams/valve or less.

Oil-soluble polyalkylene polyamines containing an olefinic polymer chain are known to improve detergent properties of fuels used in carburettor and throttle body type engines. These polyalkylene polyamines, particularly when used at high concentrations, can result in valve sticking and an increase in octane requirement. Various materials have been added to these polyalkylene polyamines to improve their performance. Thus, U.S. Patent No. 5,006,130 discloses as a gasoline additive (a) polyalkylene polyamine and (b) at least one component selected from (i) a polymer of a C₂ to C₆ monoolefin, (ii) a copolymer of a C₂ to C₆ monoolefin, (iii) the corresponding hydrogenated polymer or copolymer, and (iv) an oil soluble poly(oxyalkylene) alcohol, glycol or polyol or a mono- or di- ether thereof.

U.S. Patents Nos. 4,197,409 and 4,191,537 disclose hydrocarbyl poly(oxyalkylene) aminocarbamates as deposit control additives which effectively control deposits in intake systems (carburettor, valves, etc.) of engines operated with fuels containing them, but which do not contribute to the combustion chamber deposits which cause increased octane requirements.

Mannich polyamines comprising the condensation product of a high molecular weight alkyl-substituted hydroxyaromatic compound, an amine which contains an amino group having at least one active hydrogen atom, and an aldehyde have been disclosed in U.S. Patent No. 4,231,759 and are said to be useful for imparting detergency properties to an automotive fuel in order to keep intake valves clean.

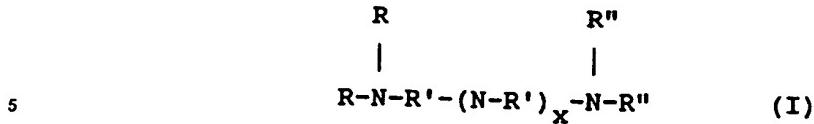
In accordance with the present invention, there is provided a gasoline composition comprising a major amount of a gasoline and from 5 ppmw to 1,000 ppmw based on the gasoline composition of a mixture of (a) an oil soluble polyamine selected from the group consisting of (i) an aliphatic alkylene polyamine containing at least one olefinic polymer chain attached to a nitrogen atom and/or a carbon atom of the alkylene radical(s) connecting the amino nitrogen atoms and said polyamine having a number average molecular weight in the range from 600 to 10,000, (ii) a Mannich polyamine comprising the condensation product of a high molecular weight sulphur-free alkyl-substituted hydroxyaromatic compound wherein the each alkyl group has a number average molecular weight in the range from 600 to 10,000, an amine which contains an amino group having at least one active hydrogen atom, and an aldehyde, wherein the respective molar ratio of reactants is 1 : 0.1-10 : 0.1-10, and (iii) mixtures of (i) and (ii); and (b) an oil soluble hydrocarbyl poly(oxyalkylene) aminocarbamate having a number average molecular weight in the range from 600 to 10,000 having at least one basic nitrogen atom wherein said hydrocarbyl group contains from 1 to 30 carbon atoms, and wherein the weight ratio of said polyamine (a) to said hydrocarbyl poly(oxyalkylene) aminocarbamate (b) ranges from 3:1 to 1:2.

Component (a) may be selected from either an aliphatic alkylene polyamine, a Mannich polyamine or mixtures of an aliphatic alkylene polyamine and a Mannich polyamine.

(i) Aliphatic Alkylene Polyamine

The oil soluble aliphatic alkylene polyamine component detergent (a)(i) has at least one polymer chain having from 500 to 9,900 M_n (number average molecular weight) and preferably from 550 to 4,900 M_n, and particularly from 600 to 1,300 M_n, and which may be saturated or unsaturated and straight or branched chain and attached to a nitrogen atom and/or a carbon atom of the alkylene radicals connecting the amino nitrogen atoms.

Preferably the aliphatic alkylene polyamine is a compound of the general formula:



where x is 0 to 5; R is selected from the group consisting of a hydrogen atom and a polyolefin group having a M_n from 500 to 9,900, at least one R being a polyolefin group; each R' independently represents a C₁-C₈, preferably C₁-C₄, alkylene group; and each R'' independently represents a hydrogen atom or a lower alkyl group. Preferred is when one R is a branched-chain olefin polymer and the other R is hydrogen. The number average molecular weight range of R is preferably 550 to 4,900 M_n , with a range of 600 to 1,300 M_n being particularly preferred.

The olefinic polymers (R) which are reacted with polyamines to form the aliphatic alkylene polyamines used in the present invention include olefinic polymers derived from alkanes or alkenes with straight or branched chains, which may or may not have aromatic or cycloaliphatic substituents, for instance, groups derived from polymers or copolymers of olefins which may or may not have a double bond. Examples of unsubstituted alkenyl and alkyl groups are polyethylene groups, polypropylene groups, polybutylene groups, polyisobutylene groups, polyethylene-polypropylene groups and the corresponding groups without double bonds. Examples of substituted alkenyl and alkyl groups are polyethylene-poly-alpha-methyl styrene groups and the corresponding groups without double bonds. Particularly preferred are polypropylene and especially polyisobutylene groups.

The R'' group may be hydrogen but is preferably lower alkyl, i.e., containing up to 7 carbon atoms, and more preferably is selected from methyl, ethyl, propyl and butyl groups.

The polyamines used to form the aliphatic alkylene polyamines used in this invention include primary and secondary aliphatic polyamines such as ethylene diamine, diethylene triamine, triethylene tetramine, hexamethylene diamine, heptamethylene diamine, diaminopentane or pentamethylene diamine, homologues up to 18 carbon atoms, N-methyl ethylene diamine, N-propyl ethylene diamine, N,N-dimethyl-1,3-propane diamine, N-2-hydroxypropyl ethylene diamine, penta-(1-methylpropylene)hexamine, tetrabutylene-pentamine, hexa-(1,1-dimethylethylene)heptane, di-(1-methylamylene)-triamine, tetra-(1,3-dimethylpropylene)pentamine, penta-(1,5-dimethylarylene)-hexamine, di(1-methyl-4-ethylbutylene)triamine, penta-(1,2-dimethyl-1-isopropyl ethylene)hexamine and tetraoctylenepentamine.

Compounds possessing triamine as well as tetramine and pentamine groups are applicable for use because these can be prepared from technical mixtures of polyethylene polyamines, which could offer economic advantages.

The polyamine can be a cyclic polyamine, for instance, the cyclic polyamines formed when aliphatic polyamines with nitrogen atoms separated by ethylene groups are heated in the presence of hydrogen chloride.

An example of a suitable process for the preparation of an aliphatic alkylene polyamine employed according to the invention is the reaction of a halogenated polyhydrocarbon having at least one halogen atom as a substituent and a hydrocarbon chain as defined hereinbefore for R, with a polyamine. The halogen atom is replaced by a polyamine group, while hydrogen halide is formed. The hydrogen halide can then be removed in any suitable way, for instance, as a salt with excess polyamine. The reaction between halogenated hydrocarbon and polyamine is preferably effected at elevated temperature in the presence of a solvent; particularly a solvent having a boiling point of at least 160°C.

The reaction between polyhydrocarbon halide and a polyamine having more than one nitrogen atom available for this reaction is preferably effected in such a way that cross-linking is reduced to a minimum, for instance, by applying an excess of polyamine.

The number average molecular weight of the aliphatic alkylene polyamine will range from 600 to 10,000 M_n , preferably from 600 to 5,000 M_n , and most preferably from 600 to 1,500 M_n .

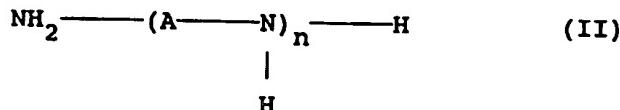
(ii) Mannich Polyamine

The oil soluble Mannich polyamine component detergent (a)(ii) comprises a condensation product of a high molecular weight alkyl-substituted hydroxyaromatic compound, an amine which contains an amino group having at least one active hydrogen atom, preferably a polyamine, and an aldehyde. Such condensation products can be prepared by condensing in the usual manner under Mannich reaction

conditions:

- (1) an alkyl-substituted hydroxyaromatic compound, in which the or each alkyl substituent has 600 to 10,000, preferably 600 to 3,000, more preferably 740 to 1,200, and most preferably 1,000 to 1,100, M_n , preferably a polyalkylphenol whose polyalkyl substituent is derived from 1-mono-olefin polymers having M_n preferably in the range from 600 to 3,000, more preferably from 740 to 1,200, and most preferably from 1,000 to 1,100;
- (2) an amine, preferably a polyamine, containing at least one $> \text{NH}$ group, preferably an alkylene polyamine of the formula

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wherein each A independently represents a divalent alkylene radical having from 2 to 6 carbon atoms and n is an integer from 1 to 10; and

- (3) an aldehyde, preferably formaldehyde.

Examples of Mannich polyamines useful in the present invention are described in U.S. Patent No. 4,231,759. The foregoing high molecular weight products employed in this invention are preferably prepared according to the conventional methods heretofore employed for the preparation of Mannich condensation products, using the above-named reactants in the respective molar ratios of high molecular weight alkyl-substituted hydroxyaromatic compound (1), amine (2) and aldehyde (3) of 1 : 0.1-10 : 0.1-10. A suitable condensation procedure involves adding, at a temperature ranging from ambient temperature (20°C) to 93°C, the aldehyde reagent (3), e.g. formaldehyde, to a mixture of reagents (1) and (2) alone or in any easily removed organic solvent, such as benzene, xylene or toluene or in solvent-refined neutral oil and then heating the reaction mixture to an elevated temperature (120-175°C) while preferably blowing with an inert stripping gas, such as nitrogen or carbon dioxide until dehydration is complete. The product so obtained is finished by filtration and dilution as desired.

The preferred detergent additives employed in this invention are high molecular weight Mannich condensation products, formed by reacting (1) an alkylphenol, whose alkyl group has 600 to 3,000 M_n ; (2) an ethylene polyamine, an amine reactant; and (3) a formaldehyde affording reactant in the respective molar ratio of 1 : 0.5-2.0 : 1.0-3.0.

Representative of the high molecular weight alkyl-substituted hydroxyaromatic compounds are polypropylphenol, polybutylphenol and other polyalkylphenols. These polyalkylphenols may be obtained by the alkylation, in the presence of an alkylating catalyst such as BF_3 , of phenol with high molecular weight polypropylene, polybutylene and other polyalkylene compounds to give one or more alkyl substituents on the benzene ring of phenol, each alkyl substituent having 600 to 10,000 M_n .

The 600 M_n and higher M_n alkyl substituents on the hydroxyaromatic compounds may be derived from high molecular weight polypropylenes, polybutenes and other polymers of mono-olefins, principally 1-monoolefins. Also useful are copolymers of mono-olefins with monomers copolymerisable therewith wherein the copolymer contains at least 90%, by weight, of mono-olefin units. Specific examples are copolymers of propylene or butenes (butene-1, butene-2 and isobutylene) with monomers copolymerisable therewith wherein the copolymer contains at least 90% by weight, of propylene and butene units, respectively. Said monomers copolymerisable with propylene or said butenes include monomers containing a small proportion of unreactive polar groups such as chloro, bromo, keto, ether, aldehyde, which do appreciably lower the oil-solubility of the polymer. The comonomers polymerised with propylene or said butenes may be aliphatic and can also contain non-aliphatic groups, e.g., styrene, methylstyrene, p-dimethylstyrene and divinylbenzene. From the foregoing limitation placed on the monomer copolymerised with propylene or said butenes, it is abundantly clear that said polymers and copolymers of propylene and said butenes are substantially aliphatic hydrocarbon polymers. Thus the resulting alkylated phenols contain substantially alkyl hydrocarbon substituents having M_n upward from 600.

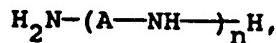
In addition to these high molecular weight hydroxyaromatic compounds others which may be used include, exclusive of sulphurised derivatives, high molecular weight alkyl-substituted derivatives of resorcinol, hydroquinone, cresol, catechol, xylanol, hydroxy diphenyl, benzylphenol, phenethylphenol, naphthol and tolylnaphthol. Preferred for the preparation of such preferred Mannich condensation products are the polyalkylphenol reactants, e.g., polypropylphenol and polybutylphenol whose alkyl groups have 600 to 3,000

M_n , the more preferred alkyl groups having 740 to 1,200 M_n , while the most preferred alkyl group is a polypropyl group having 800 to 850 M_n , especially 825 M_n .

The preferred configuration of the alkyl-substituted hydroxyaromatic compound is that of a para-substituted mono-alkylphenol. However, any alkylphenol readily reactive in the Mannich condensation reaction may be employed. Accordingly, ortho mono-alkylphenols and dialkylphenols are suitable for use in this invention.

Various amine reactants may be utilised including mono and polyamines. The preferred amine reactants are alkylene polyamines, principally polyethylene polyamines. Other representative organic compounds containing at least one $>\text{NH}$ group suitable for use in the preparation of Mannich condensation products are well known and include the mono- and di-amino alkanes and their substituted analogues, e.g., ethylamine, dimethylamine, dimethylaminopropylamine and diethanol amine; aromatic diamines, e.g., phenylene diamine, diamino naphthalenes; heterocyclic amines, e.g., morpholine, pyrrole, pyrrolidine, imidazole, imidazolidine, and piperidine; melamine and their substituted analogues.

Suitable alkylene polyamine reactants include ethylenediamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, hexaethylene heptamine, heptaethylene octamine, octaethylene nonamine, nonaethylene decamine, decaethylene undecamine and mixtures of such amines having nitrogen contents corresponding to the alkylene polyamines, in the formula (II)



mentioned before, where A is divalent ethylene and n is an integer from 1 to 10. Corresponding propylene polyamines such as propylene diamine and di-, tri-, tetra-, penta-propylene tri-, tetra-, penta- and hexaamines are also suitable reactants. The alkylene polyamines are usually obtained by the reaction of ammonia and dihalo alkanes, such as dichloro alkanes. Thus the alkylene polyamines obtained from the reaction of 2 to 11 moles of ammonia with 1 to 10 moles of dichloro alkanes having 2 to 6 carbon atoms and the chlorines on different carbons are suitable alkylene polyamine reactants.

Representative aldehydes for use in the preparation of the high molecular products used in this invention include the aliphatic aldehydes such as formaldehyde (including paraformaldehyde), acetaldehyde and aldol (b-hydroxybutyraldehyde). Formaldehyde or a formaldehyde-yielding reactant is preferred.

(iii) Mixtures of the Aliphatic Alkylene Polyamine and the Mannich Polyamine

35 Mixtures of components (a)(i) and (a)(ii) may also be suitably combined with component (b) to prepare the gasoline compositions according to the present invention.

Component (b) - Aminocarbamate

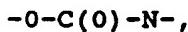
The amine moiety of the hydrocarbyl-terminated poly(oxyalkylene) aminocarbamate is preferably derived from a polyamine having from 2 to 12 amine nitrogen atoms and from 2 to 40 carbon atoms. The polyamine is preferably reacted with a hydrocarbyl poly(oxyalkylene) chloroformate to produce the hydrocarbyl poly(oxyalkylene) aminocarbamate component (b). The chloroformate is itself derived from hydrocarbyl poly(oxyalkylene) alcohol by reaction with phosgene. The polymer, encompassing diamines, provides the product poly(oxyalkylene) aminocarbamate with, on average, at least one basic nitrogen atom per carbamate molecule, i.e., a nitrogen atom titratable by strong acid. The polyamine preferably has a carbon-to-nitrogen ratio in the range from 1:1 to 10:1. The polyamine may be substituted with substituents selected from hydrocarbyl groups having from 1 to 10 carbon atoms, acyl groups having from 2 to 10 carbon atoms, and monoketone, monohydroxy, mononitro, monocyno, alkyl and alkoxy derivatives of hydrocarbyl groups having from 1 to 10 carbon atoms. It is preferred that at least one of the basic nitrogen atoms of the polyamine is a primary or secondary amino nitrogen. Examples of suitable polyamines are those described in U.S. Patent No. 4,191,537.

Hydrocarbyl, as used in describing all the components of this invention, denotes an organic radical composed of carbon and hydrogen which may be aliphatic, alicyclic, aromatic or combination thereof, e.g., aralkyl. Preferably, the hydrocarbyl group will be relatively free of aliphatic unsaturation, i.e., ethylenic and acetylenic, particularly acetylenic unsaturation. The more preferred polyamine for the aminocarbamate component is a polyalkylene polyamine, including alkylene diamine, and including substituted polyamines, e.g., alkyl and hydroxylalkyl-substituted polyalkylene polyamine. Preferably, the alkylene group contains from 2 to 6 carbon atoms, there being preferably from 2 to 3 carbon atoms between the nitrogen

atoms. Examples of such polyamines include ethylenediamine, diethylene triamine, triethylene tetramine, dipropylene triamine and tetraethylene pentamine. Among the polyalkylene polyamines, polyethylene polyamines and polypropylene polyamines containing 2-12 amine nitrogen atoms and 2-24 carbon atoms are especially preferred, with the lower polyethylene/polypropylene polyamines, e.g. ethylenediamine and dipropylene triamine, being most preferred.

The hydrocarbyl-terminated poly(oxyalkylene) polymers which are utilised in preparing the aminocarbamates are monohydroxy compounds, e.g., alcohols, often termed monohydroxy polyethers, or polyalkylene glycol monocarbonyl ethers, or "capped" poly(oxyalkylene) glycols, and are to be distinguished from the poly(oxyalkylene) glycols (diols), or polyols, which are not hydrocarbyl-terminated, i.e., are not capped. The hydrocarbyl-terminated poly(oxyalkylene) alcohols are produced by the addition of lower alkylene oxides, such as ethylene oxide, propylene oxide and butylene oxide to the hydroxy compound ROH under polymerisation conditions, wherein R is the hydrocarbyl group which caps the poly(oxyalkylene) chain. In the poly(oxyalkylene) component of the aminocarbamate, the group R will contain from 1 to 30 carbon atoms, preferably from 2 to 20 carbon atoms and is aliphatic or aromatic, i.e. an alkyl or alkylphenyl wherein the alkyl is a straight or branched-chain of from 1 to 24 carbon atoms. The oxyalkylene units in the poly(oxyalkylene) component preferably contain from 2 to 5 carbon atoms but one or more units of a larger carbon number may also be present. Each poly(oxyalkylene) polymer contains at least 5 oxyalkylene units, preferably 8 to 100 oxyalkylene units, more preferably 10 to 100 units and most preferably 10 to 25 such units. The poly(oxyalkylene) component is more fully described and exemplified in U.S. Patents Nos. 4,191,537 and 4,197,409. The hydrocarbyl poly(oxyalkylene) aminocarbamate used in the compositions of the present invention is obtained by linking the amine component and the poly(oxyalkylene) component together through a carbamate linkage, i.e.,

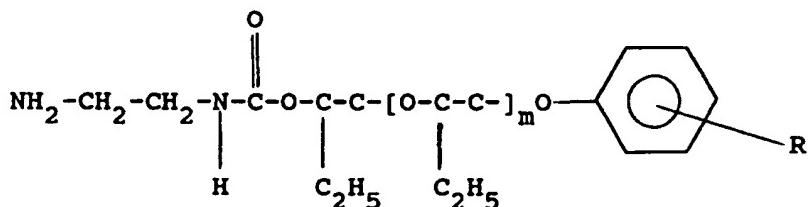
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wherein the oxygen may be regarded as the terminal hydroxyl oxygen of the poly(oxyalkylene) alcohol component, and the carbonyl group, -C(O)-, is preferably provided by a coupling agent, e.g., phosgene. In the preferred method of preparation the hydrocarbyl poly(oxyalkylene) alcohol is reacted with phosgene to produce a chloroformate and the chloroformate is reacted with the polyamine. The carbamate linkages are formed as the poly(oxyalkylene) chains are bound to the nitrogen of the polyamine through the oxycarbonyl group of the chloroformate. Since there may be more than one nitrogen atom of the polyamine which is capable of reacting with the chloroformate, the aminocarbamate contains at least one hydrocarbyl poly(oxyalkylene) polymer chain bonded through an oxycarbonyl group to a nitrogen atom of the polyamine, but the carbamate may contain 1, 2 or more such chains. It is preferred that the hydrocarbyl poly(oxyalkylene) aminocarbamate product contains, on average, 1 poly(oxyalkylene) chain per molecule (i.e., is a monocarbamate), although it is understood that this reaction route may lead to mixtures containing appreciable amounts of di- or higher poly(oxyalkylene) chain substitution on a polyamine containing several reactive nitrogen atoms. Several especially preferred aminocarbamates are butyl-poly(oxyalkylene)-N-(2-aminoethyl) carbamate and alkylphenyl-poly(oxyalkylene)-N-(2-aminoethyl) carbamate. A particularly preferred carbamate can be expressed by the following formula:

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55 wherein R is a hydrogen atom or an alkyl group and m is greater than 5. Aminocarbamates suitable for use in the present invention can be obtained from the Oronite Additives Division of Chevron Chemical Company.

Synthetic methods to avoid higher degrees of substitution, methods of preparation, and other characteristics of the aminocarbamates used as component (b) are more fully described and exemplified in U.S.

Patents Nos. 4,191,537 and 4,197,409.

The number average molecular weight of the aminocarbamate will range from 600 to 10,000 M_n, preferably from 600 to 5,000 M_n and most preferably from 600 to 2,000 M_n.

The total amount of component (a) plus component (b) present in the gasoline compositions of the invention will range from 5 to 1,000, preferably from 50 to 1,000, more preferably from 50 to 500 and even more preferably from 100 to 400 and most preferably from 200 to 300 parts per million by weight (ppmw) based on the gasoline composition. The weight ratio, component (a) component (b), will range from 3:1 to 1:2 and preferably from 2:1 to 2:3. In a particularly preferred embodiment the weight ratio is 1:1.

Suitable liquid hydrocarbon fuels in the gasoline boiling range are mixtures of hydrocarbons having a boiling point in the range from 25°C to 232°C and comprise mixtures of saturated hydrocarbons, olefinic hydrocarbons and aromatic hydrocarbons. Preferred are gasoline blends having a saturated hydrocarbon content ranging from 40 to 80 per cent volume, an olefinic hydrocarbon content ranging from 0 to 30 per cent volume and an aromatic hydrocarbon content ranging from 10 to 60 per cent volume. The base fuel can be derived from straight run gasoline, polymer gasoline, natural gasoline, dimer or trimerised olefins, synthetically produced aromatic hydrocarbon mixtures from thermally or catalytically reformed hydrocarbons, or from catalytically cracked or thermally cracked petroleum stocks, or mixtures of these. The hydrocarbon composition and octane level of the base fuel are not critical. The octane level, (R+M)/2, will generally be above 85. Any conventional motor fuel base may be employed in the practice of this invention. For example, in the gasoline, hydrocarbons can be replaced by up to substantial amounts of conventional alcohols, or ethers, conventionally known for use in fuels. The base fuels are desirably substantially free of water, since water could impede a smooth combustion.

Preferably, the gasolines used in the present invention are lead-free, but can contain minor amounts of blending agents such as methanol, ethanol and methyl tertiary butyl ether e.g., from 0.1 to 15% volume of the base fuel. The gasolines can also contain antioxidants such as phenolics, e.g., 2,6-di-tert-butylphenol or 25 phenylenediamines, e.g., N,N'-di-sec-butyl-p-phenylenediamine, dyes, metal deactivators and dehazers such as polyester-type ethoxylated alkylphenol-formaldehyde resins. Corrosion inhibitors, such as a polyhydric alcohol ester of a succinic acid derivative having on at least one of its alpha-carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group having 20 to 500 carbon atoms, for example, pentaerythritol diester of polyisobutylene-substituted succinic acid, the polyisobutylene group having a number average molecular weight of 950, in an amount of 1 to 1,000 ppmw. The gasolines may also contain antiknock compounds such as a methyl cyclopentadienylmanganese tricarbonyl and ortho-azidophenol as well as co-antiknock compounds such as benzoylacetone.

The additive mixture (a) plus (b) used in the present invention can be added to the gasoline neat or in the form of a concentrate. For example, the agent can be added separately to the gasoline or blended with other additives. Accordingly, the present invention further provides a gasoline additive concentrate comprising a major amount of a mixture of (a) an oil soluble polyamine selected from the group consisting of (i) an aliphatic alkylene polyamine containing at least one olefinic polymer chain attached to a nitrogen atom and/or a carbon atom of the alkylene radical(s) connecting the amino nitrogen atoms and said polyamine having a number average molecular weight in the range from 600 to 10,000, (ii) a Mannich polyamine comprising the condensation product of a high molecular weight sulphur-free alkyl-substituted hydroxyaromatic compound wherein the or each alkyl group has a number average molecular weight in the range from 600 to 10,000, an amine which contains an amino group having at least one active hydrogen atom, and an aldehyde, wherein the respective molar ratio of reactants is 1 : 0.1-10 : 0.1-10, and (iii) mixtures of (i) and (ii); and (b) an oil soluble hydrocarbyl poly(oxyalkylene) aminocarbamate having a number average molecular weight in the range from 600 to 10,000 having at least one basic nitrogen atom wherein said hydrocarbyl group contains from 1 to 30 carbon atoms, and wherein the weight ratio of said polyamine (a) to said hydrocarbyl poly(oxyalkylene) aminocarbamate (b) ranges from 3:1 to 1:2, and a minor amount of a gasoline compatible diluent, e.g. a gasoline compatible diluent boiling in the range from 50 to 232°C. The additive mixture (a) plus (b) can be added to the gasoline at any point prior to its delivery to the end user.

The present invention still further provides the use of from 5 ppmw to 1,000 ppmw based on total composition of a mixture of (a) an oil soluble polyamine selected from the group consisting of (i) an aliphatic alkylene polyamine containing at least one olefinic polymer chain attached to a nitrogen atom and/or a carbon atom of the alkylene radical(s) connecting the amino nitrogen atoms and said polyamine having a number average molecular weight in the range from 600 to 10,000, (ii) a Mannich polyamine comprising the condensation product of a high molecular weight sulphur-free alkyl-substituted hydroxyaromatic compound wherein the or each alkyl group has a number average molecular weight in the range from 600 to 10,000, an amine which contains an amino group having at least one active hydrogen atom, and an aldehyde, wherein the respective molar ratio of reactants is 1 : 0.1-10 : 0.1-10, and (iii) mixtures of (i) and (ii); and (b)

an oil soluble hydrocarbyl poly(oxyalkylene) aminocarbamate having a number average molecular weight in the range from 600 to 10,000 having at least one basic nitrogen atom wherein said hydrocarbyl group contains from 1 to 30 carbon atoms, and wherein the weight ratio of said polyamine (a) to said hydrocarbyl poly(oxyalkylene) aminocarbamate (b) ranges from 3:1 to 1:2, in a gasoline composition comprising a major amount of a gasoline, to achieve a reduction in intake valve deposits.

5 The invention will be further understood from the following illustrative examples.

Example I

10 This example illustrates the beneficial effect on intake valve deposits of a gasoline additive comprising a mixture of an aliphatic alkylene polyamine and a hydrocarbyl poly(oxyalkylene) aminocarbamate.

Intake valve deposit tests were conducted in a BMW 325 car equipped with the 2.7-litre, six-cylinder engine with port fuel injection, and was operated for 8,050 kilometres on the test fuel. Before the test started, deposits were removed from the cylinder head, intake manifold and piston tops and new intake valves were weighed and installed. The oil and filter were changed, new spark plugs installed and the fuel injectors flow checked. Mileage was accumulated on a road simulation dynamometer. A four minute test cycle was employed. It consisted of a 2 minute acceleration from 54 to 75 km/hr, a 1 minute acceleration to 112 km/hr and a 1 minute deceleration to 54 km/hr. The average speed was 79 km/hr and the cycle was repeated until 8050 kilometres were accumulated (almost 102 hrs).

20 Table 1 lists the additive compositions A to C, 1 and 2 used in premium unleaded base gasolines and the average (of six) intake valve deposit weights at the end of the test (8,050 kilometres). Compositions A, B and C are comparative compositions whilst compositions 1 and 2 are in accordance with the present invention.

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Table 1

Composition	Component (a)(i) ¹ ppmw	Component (b) ² ppmw	Ratio (a)/(b)	BMW 325 Results Avg. Deposit Weight,mg
A	200	0	200:0	39.0
1	150	50	3:1	34.3
2	100	100	1:1	34.6
B	50	150	1:3	148.6
C	0	200	0:200	153.6

30 ¹ Component (a)(i) is N-polyisobutetyl-N',N'-dimethyl-1,3-diaminopropane. M_n = 1050.

² Component (b) is a hydrocarbyl poly(oxyalkylene) aminocarbamate obtained from the Oronite Additives Division of Chevron Chemical Company as OGA 480. M_n = 1400-1800.

40 The results of these tests demonstrate that the gasoline compositions of the invention provide a synergistic improvement in intake valve deposit reduction while concomitantly allowing for the reduction in the amount of aliphatic alkylene polyamine thereby lessening the known effect of the polyamine to cause valve sticking.

45 Example II

Intake valve deposit tests were conducted in a BMW 318i car equipped with the 1.8-litre, four-cylinder engine which was operated for 10,000 miles (16,093.4 kilometres) on the test fuel. Before the test started, deposits were removed from the cylinder head, intake manifold and piston tops and new intake valves were weighed and installed. The oil and filter were changed, new spark plugs installed and the fuel injectors flow checked. Mileage was accumulated on public roads using trained drivers. The test route consisted of about 10% city driving, 20% on secondary roads and 70% highway driving (maximum speed of 65 mph (104.6 km/h)).

The primary test data was the intake valve deposit (IVD) weights at the end of the 10,000-mile (16,093.4-kilometre) test. BMW's pass criteria are as follows: an average deposit weight of 100 milligrams/valve or less at the conclusion of the test meets BMW requirements for unlimited mileage acceptance; an average deposit weight of 250 mg/valve or less at the conclusion of the test meets BMW's requirement for 50,000-mile (80,467-kilometre) service.

Table 2 lists the additive compositions 3 and 4 used in regular unleaded base gasolines and the average intake deposit weights at the end of the test (10,000 miles/16,093.4 kilometres). Compositions 3 and 4 are in accordance with the present invention.

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Table 2

	Composition	Component (a) ppmw	Component (b) ppmw	Ratio (a)/(b)	BMW 318i Results Avg. Deposit Weight, mg
10	3	125 ¹	125 ²	1:1	0
	4	125 ³	125 ²	1:1	44

- ¹ Component (a) is the Amoco Mannich Amine known as "Amoco 596" described in U.S. Patent No. 4,231,759. $M_n = 1000-1100$.
- ² Component (b) is a hydrocarbyl poly(oxyalkylene) aminocarbamate, $M_n = 1400-1800$, obtained from the Oronite Additives Division of Chevron Chemical Company as OGA 480.
- ³ Component (a) is N-polyisobutetyl-N'-N'-dimethyl-1,3-diaminopropane. $M_n = 1050$.

20 Claims

1. A gasoline composition comprising a major amount of a gasoline and from 5 ppmw to 1,000 ppmw based on the gasoline composition of a mixture of (a) an oil soluble polyamine selected from the group consisting of (i) an aliphatic alkylene polyamine containing at least one olefinic polymer chain attached to a nitrogen atom and/or a carbon atom of the alkylene radical(s) connecting the amino nitrogen atoms and said polyamine having a number average molecular weight in the range from 600 to 10,000, (ii) a Mannich polyamine comprising the condensation product of a high molecular weight sulphur-free alkyl-substituted hydroxyaromatic compound wherein the or each alkyl group has a number average molecular weight in the range from 600 to 10,000, an amine which contains an amino group having at least one active hydrogen atom, and an aldehyde, wherein the respective molar ratio of reactants is 1 : 0.1-10 : 0.1-10, and (iii) mixtures of (i) and (ii); and (b) an oil soluble hydrocarbyl poly(oxyalkylene) aminocarbamate having a number average molecular weight in the range from 600 to 10,000 having at least one basic nitrogen atom wherein said hydrocarbyl group contains from 1 to 30 carbon atoms, and wherein the weight ratio of said polyamine (a) to said hydrocarbyl poly(oxyalkylene) aminocarbamate (b) ranges from 3:1 to 1:2.
2. A composition according to claim 1, wherein the aliphatic alkylene polyamine has a molecular weight in the range from 600 to 5,000, the or each alkyl group of the Mannich polyamine has a molecular weight in the range from 600 to 3,000, and the aminocarbamate has a molecular weight in the range from 600 to 5,000.
3. A composition according to claim 1 or claim 2, wherein the aliphatic alkylene polyamine has a molecular weight in the range from 600 to 1,500, the or each alkyl group of the Mannich polyamine has a molecular weight in the range from 1,000 to 1,100, and the aminocarbamate has a molecular weight in the range from 600 to 2,000.
4. A composition according to any one of claims 1 to 3, wherein the amount of the mixture of polyamine and aminocarbamate ranges from 50 ppmw to 500 ppmw based on the gasoline composition.
5. A composition according to claim 4, wherein the amount of the mixture of polyamine and aminocarbamate ranges from 100 ppmw to 400 ppmw based on the gasoline composition.
6. A composition according to claim 5, wherein the amount of the mixture of polyamine and aminocarbamate ranges from 200 ppmw to 300 ppmw based on the gasoline composition.
7. A composition according to any one of the preceding claims, wherein the weight ratio of polyamine to aminocarbamate ranges from 2:1 to 2:3.

8. A composition according to claim 7, wherein the weight ratio of polyamine to aminocarbamate is 1:1.
9. A gasoline additive concentrate comprising a major amount of a mixture of (a) an oil soluble polyamine selected from the group consisting of
 - 5 (i) an aliphatic alkylene polyamine containing at least one olefinic polymer chain attached to a nitrogen atom and/or a carbon atom of the alkylene radical(s) connecting the amino nitrogen atoms and said polyamine having a number average molecular weight in the range from 600 to 10,000,
 - (ii) a Mannich polyamine comprising the condensation product of a high molecular weight sulphur-free alkyl-substituted hydroxyaromatic compound wherein the or each alkyl group has a number average molecular weight in the range from 600 to 10,000, an amine which contains an amino group having at least one active hydrogen atom, and an aldehyde, wherein the respective molar ratio of reactants is 1 : 0.1-10 : 0.1-10, and
 - 10 (iii) mixtures of (i) and (ii); and (b) an oil soluble hydrocarbyl poly(oxyalkylene) aminocarbamate having a number average molecular weight in the range from 600 to 10,000 having at least one basic nitrogen atom wherein said hydrocarbyl group contains from 1 to 30 carbon atoms, and wherein the weight ratio of said polyamine (a) to said hydrocarbyl poly(oxyalkylene) aminocarbamate (b) ranges from 3:1 to 1:2, and a minor amount of a gasoline compatible diluent.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 20 2889

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.S)
X	WO-A-9 112 303 (CHEVRON) * the whole document * ---	1-9	C10L1/22
D,Y	US-A-4 191 537 (LEWIS ET AL.) * column 10, line 52 - line 56 * ---	1-9	
D,Y	US-A-4 231 759 (UDELHOFEN ET AL.) * the whole document * ---	1-9	
Y	GB-A-2 010 324 (CHEVRON) * the whole document * ---	1-9	
D,A	US-A-5 006 130 (AIELLO ET AL.) * the whole document * -----	1-9	
TECHNICAL FIELDS SEARCHED (Int. CL.S)			
C10L			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	22 OCTOBER 1992	DE LA MORINERIE	
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